



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Shuichi KANNO et al.

Serial No. 09/005,006

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For: PROCESS FOR TREATING FLUORINE COMPOUND-  
CONTAINING GAS

D E C L A R A T I O N

COMMISSIONER FOR PATENTS  
Washington, D. C. 20231

Sir:

I, Shuichi Kanno, a Japanese citizen residing at 17-13, Ishinazaka-cho, 1-chome, Hitachi-shi, Ibaraki, Japan do hereby solemnly and sincerely declare THAT:

I graduated from the graduate course of Engineering Department (majoring in material chemistry) of Tohoku University in March, 1992;

I began employment with Hitachi, Ltd., the assignee of the above-identified application in April, 1992 and have been engaged in said company, since that time, in the study of catalysts for chemical reactions;

BEST AVAILABLE COPY

I am the first-named inventor of the above-identified application and am well aware of the prosecution history thereof;

I conducted the following Experiments in order to know how long the catalyst of Rossin et al (US Patent No. 6,069,291) can maintain high conversion rate, that is, the durability of the catalyst of Rossin et al.

[PREPARATION OF CATALYST]

A catalyst comprising aluminum oxide, cobalt and zirconia was prepared by the method disclosed in Example XVI of USP 6,069,291.

In a 5-liter beaker, 1.5 liters of deionized water was placed and stirred with a laboratory scale mixer. Then, 1001.16 of pseudoboehmite (G250, manufactured by Alcoa Inc.) was added to the stirring deionized water. Since the stirring became impossible during the addition of deionized water, 500 ml of deionized water was further added to conduct stirring again.

(Reasons for stopping of stirring seemed to be an increase of viscosity caused by polymerization. The addition of deionized water was based on my original idea derived from abundant experiments.)

After addition of whole amount of the pseudo-boehmite, the stirring became almost impossible due to an increase of the viscosity, so that 200 ml of deionized water was further added. The resulting aqueous solution had a pH of 9.0.

Then, to the resulting aqueous solution, a zirconium oxynitrate solution was added. After the addition, pH became 5.39.

The zirconium oxynitrate solution was prepared by dissolving 45.67 g of zirconium oxynitrate reagent manufactured by Soekawa Rika in 59.52 g of deionized water.

During the preparation for dropping nitric acid after the addition of the zirconium oxynitrate solution, the stirring was stopped due to an increase of the viscosity. Thus, 1100 ml of deionized water was added thereto.

Then, nitric acid was dropped to adjust the pH of the solution 3.3.

Stirring was continued for a whole day under such conditions. Then, after stopping the stirring, the solution was aged for three days. After completion of the aging, the contents were removed to an evaporating dish to dry at 125°C for 5 hours.

After drying, the dried product was put in a crucible and heated to 535°C at a rate of 7°C/min, followed by calcining for 2 hours.

The calcined Zr/Al catalyst at 535°C was crushed in a mortal and sieved using a 6.5/12 mesh sieve, followed by drying at 125°C for 0.5 hour.

Thus obtained Zr/Al catalyst in an amount of 200.81 g was impregnated in an aqueous solution of Co.

The Co aqueous solution was prepared by dissolving 60.02 g of triethanolamine and 112.61 g of cobalt acetate tetrahydrate in 300 ml of deionized water. The cobalt acetate tetrahydrate in an amount of 112.61 g is equal to 80.06 g of cobalt acetate.

In the course of impregnation in the Co aqueous solution, it was impossible to impregnate the whole solution at a time. Thus, impregnation was conducted for several times. That is, after dipping, the product was dried at 120°C for 10 to 15 minutes, followed by impregnating in the Co aqueous solution. Repeating such a procedure for several times, when the Co aqueous solution was lost, drying was conducted at 120°C for 2 hours, followed by calcining at 450°C to prepare a Co/Zr/Al catalyst.

[DECOMPOSITION OF  $C_2F_6$ ]

Conversion of  $C_2F_6$  was conducted according to the method described in EXAMPLE XVII of USP 6,069,291. The employed gas concentration was 500 ppm as disclosed in EXAMPLE XVII and 5000 ppm conventionally used in the treatment of semiconductor devices.

**Experiment 1 (500 ppm)**

The above-mentioned Co/Zr/Al catalyst in 6.5/12 mesh in an amount of 41.28 g (considering the size of a reaction tube) was used. The reaction gas composition was 470 ppm of  $C_2F_6$ , 3.2% by volume of  $H_2O$ , and balance being air. The gas hourly space velocity (SV) was  $1800\text{ hr}^{-1}$  and the temperature was  $700^\circ\text{C}$ .

**Experiment 2 (5000 ppm)**

The above-mentioned Co/Zr/Al catalyst in 6.5/12 mesh in an amount of 39.953 g was used. The reaction gas composition was 5000 ppm of  $C_2F_6$ , 32% by volume of  $H_2O$  (due to use of  $C_2F_6$  concentration 10 times as large as Experiment 1), and balance being air. The gas hourly space velocity (SV) was  $1800\text{ hr}^{-1}$  and the temperature was  $700^\circ\text{C}$ .

**[RESULTS]**

Attached Fig. 1 shows a relation between the

conversion rate of  $C_2F_6$  at the concentration of 500 ppm and the reaction time.

Attached Fig. 2 shows a relation between the conversion rate of  $C_2F_6$  at the concentration of 5000 ppm and the reaction time.

As shown in Fig. 1, the Co/Zr/Al catalyst of Rossin et al shows high conversion rate of 99% to near 100% for 0 to 2000 hours, when the  $C_2F_6$  concentration was as low as 500 ppm.

On the other hand, when the  $C_2F_6$  concentration was as high as 5000 ppm, the conversion rate of  $C_2F_6$  immediately after the reaction was as relatively low as about 80%, and the conversion rate was lowered with the lapse of time without improving the ability, and lowered to about 60% after 100 hours, and about 35% after 170 hours, as shown in Fig. 2.

The undersigned declarant declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are

punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 12th day of September, 2003.

Shunichi Kanno

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